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Intramolecular NH/π Complexes of 2-Allylaniline Derivatives in the Ground and Excited States

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The photochemical and photophysical properties of three 8-allyl-1,2,3,4-tetrahydroquinolines (**1a**−**c**) have been studied. These compounds exhibit a 2-allylaniline-like photochemical behavior, undergoing photocyclization to lilolidines (**3a**−**c**). The absorption, emission, and excitation spectra of **1a**−**c**, employing convenient model compounds for comparison, demonstrate the formation of a NH/π intramolecular ground-state complex (AB). This species can absorb light at long wavelengths (330−340 nm), giving rise to the corresponding excited complex AB*. Emission from AB* is red-shifted (420 nm) with respect to that observed when the monomer A is excited ($\lambda_{\text{exc}} = 300$ nm). These experimental results have been rationalized by means of density-funtional theory calculations.

Introduction

The photochemistry of 2-allylanilines has attracted considerable attention for the last three decades.[1−9] The main photoreaction reported is photocyclization to five- and/or six-membered ring compounds (Scheme 1), depending on the allyl substitution.

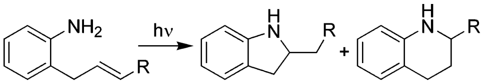
It was initially suggested that the photoprocess occurs via intramolecular electron transfer, with involvement of the first excited singlet state. This hypothesis has recently been confirmed by photochemical and photophysical studies on N-acyl derivatives.[8] The primary charge-separated intermediates undergo intramolecular proton transfer, leading to biradicals which immediately collapse to the final cyclic products (Scheme 2).

As the amino group and the allyl system are the two substructures participating in photocyclization, their intramolecular interaction (both in the ground and in the excited states) should be a key factor influencing the photophysical and photochemical properties of this group of compounds. Such interaction has been evidenced by IR spectroscopy and theoretically analyzed by semiempirical calculations.[10,11] Similar studies have been performed on the OH/π interaction in 2-allylphenols.[11−13]

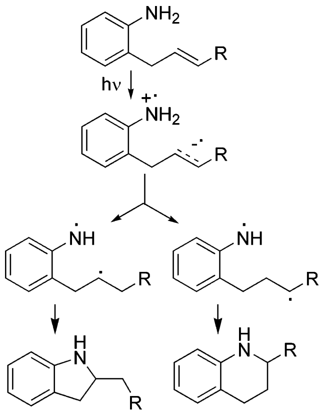
To our knowledge, the photophysical characterization of the XH/π-associated species constitutes a matter of further investigation. Thus, it would be interesting to know whether this type of species exhibit characteristic absorption bands allowing their selective excitation. If so, their emission properties could be different from those of the isolated aniline-like chromophore, in the case that some XH/π association remains in the excited state.

The aim of the present work has been to undertake a systematic investigation of this problem by means of fluorescence measurements looking at both the emission and the excitation spectra. To limit the conformational freedom of the amino group, 8-allyl-1,2,3,4-tetrahydroquinolines **1a**−**c** (Chart 1) have been selected as substrates.

SCHEME 1



SCHEME 2



As a result of this effort, we have found evidence for a ground-state complex (AB in Scheme 3) that upon light absorption gives rise to an excited species (AB*). The spectra of these species (excitation of AB and emission of AB*) are considerably red-shifted with respect to those of model compounds unable to participate in intramolecular NH/π interactions. The existence of such a ground-state complex and its lower excitation energy are supported by density-functional theory (DFT) theoretical calculations.

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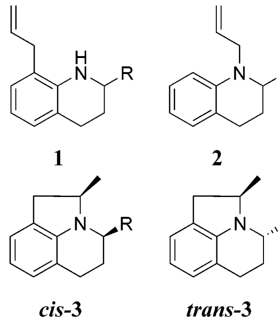
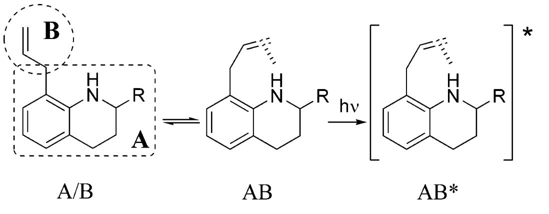
CHART 1



a R = H
b R = Me
c R = Ph

SCHEME 3



Experimental Section

Chemicals. Compounds **1a**−**c** (see structures in Chart 1) were obtained through amino-Claisen rearrangement of **2a**−**c** with $ZnCl_2$ in *p*-xylene at 130 °C, following a previously described procedure.[14] 1-Allyl-2-alkyl-1,2,3,4-tetrahydroquinolines **2a**−**c** were prepared by reaction between 2-alkyl-1,2,3,4-tetrahydroquinolines and allyl bromide, employing the standard method.[3] Compounds **3a**−**c** were obtained as described in the general irradiation procedure.

Isolation and purification were done by conventional column chromatography on silica gel, using hexane/dichloromethane as eluent, or by means of isocratic high-performance liquid chromatography (HPLC) with a semipreparative column, using hexane/ethyl acetate as eluent.

Compounds **1a**,[15] **1c**,[9] **2a**,[15] **2c**,[9] **3a**,[16] ***cis*-3c**,[9] and ***trans*-3c**[9] were known, and their structures were confirmed by comparison with the spectroscopic data reported in the literature. The unknown compounds were fully characterized by ^{1}H and ^{13}C NMR spectra, which were recorded at 300 and 75 MHz, respectively. The relative arrangement of the substituents for **3b** (trans or cis) was unambiguously determined by means of nuclear Overhauser effect (NOE) measurements (see Supporting Information).

General Irradiation Procedure. Thoroughly deoxygenated solutions of 100 mg of the substrate in 100 mL of HPLC-grade acetonitrile were irradiated at room temperature through quartz with a multilamp photoreactor, equipped with eight lamps with a maximum emission at 254 nm (monochromatic) or 300 nm (Gaussian distribution). The reaction course was followed by means of gas chromatography mass spectroscopy (GC/MS) and ^{1}H NMR. Photoreaction quantum yields were determined using phenylglyoxylic acid as actinometer.[17]

Fluorescence Measurements. Emission and excitation spectra were recorded on a standard spectrofluorimeter provided with a monochromator in the 200−900-nm wavelength range. The samples were placed into 10×10 mm^2 Suprasil quartz cells with a septum cap. The solutions were purged with argon for 15 min before measurements. The absorbance of the samples at the excitation wavelength was kept below 0.3.

Computational Methods. DFT calculations were carried out using the B3LYP[18] exchange-correlation functional, together with the standard 6-31G** and 6-31+G** basis set.[19] In addition, HF/6-31G**, HF/6-31+G**, and MP2/6-31G** optimizations were performed.[19] The optimizations were carried out using the Berny analytical gradient optimization method.[20] All calculations were carried out with the Gaussian 98 suite of programs.[21] Vertical energies of the singlet-excited state were calculated using the time-dependent (TD) DFT method.[22]

8-Allyl-2-methyl-1,2,3,4-tetrahydroquinoline (1b). ^{1}H NMR (δ, ppm): 1.17 (d, *J* 6.0 Hz, 3H), 1.45−1.61 (m, 1H), 1.82−1.93 (m, 1H), 2.65−2.90 (m, 2H), 3.20 (d, *J* 6.0 Hz, 2H), 3.40 (m, 1H), 3.70 (m, 1H), 5.03−5.17 (m, 2H), 5.83−6.00 (m, 1H), 6.56 (t, *J* 7.0 Hz, 1H), 6.79−6.89 (m, 2H). ^{13}C NMR (δ, ppm): 23.1 (CH_3), 27.4 (CH_2), 30.3 (CH_2), 36.7 (CH_2), 47.7 (CH), 116.4 (CH_2), 116.9 (CH), 121.4 (C), 122.8 (C), 127.9 (CH), 128.1 (CH), 136.7 (CH), 143.3 (C). MS (*m*/*z*, (%)): 187 (65), 172 (100). Exact mass (EI): Calcd for $C_{13}H_{17}N$: 187.1361 (M^+). Found: 187.1366.

1-Allyl-2-methyl-1,2,3,4-tetrahydroquinoline (2b). ^{1}H NMR (δ, ppm): 1.14 (d, *J* 6.5 Hz, 3H), 1.70−1.95 (m, 2H), 2.60−2.90 (m, 2H), 3.48 (m, 1H), 3.75−3.98 (m, 2H), 5.07−5.24 (m, 2H), 5.84 (m, 1H), 6.47−6.58 (m, 2H), 6.92−7.06 (m, 2H). ^{13}C NMR (δ, ppm): 19.7 (CH_3), 24.5 (CH_2), 28.6 (CH_2), 52.9 + 52.5 (CH + CH_2), 111.5 (CH), 115.9 + 115.6 (CH_2 + CH), 122.1 (C), 127.4 (CH), 129.2 (CH), 135.2 (CH), 144.9 (C). MS (*m*/*z*, (%)): 187 (32), 172 (100), 130 (32). Exact mass (EI): Calcd for $C_{13}H_{17}N$: 187.1361 (M^+). Found: 187.1357.

***cis*-2-Methyl-4-methyl-1,2,3,4-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (*cis*-3b).** ^{1}H NMR (δ, ppm): 1.24 (d, *J* 6.5 Hz, 3H), 1.44 (d, *J* 6.0 Hz, 3H), 1.65−1.85 (m, 2H), 2.56−2.68 (m, 3H), 2.98−3.12 (m, 2H), 3.53−3.65 (m, 1H), 6.57 (t, *J* 7.5 Hz, 1H), 6.81 (d, *J* 7.5 Hz, 1H), 6.87 (d, *J* 7.5 Hz, 1H). ^{13}C NMR (δ, ppm): 22.7 (CH_3), 23.5 (CH_3), 30.8 (CH_2), 38.8 (CH_2), 43.0 (CH_2), 52.5 (CH), 63.4 (CH), 117.8 (CH), 119.9 (C), 121.8 (CH), 126.2 (CH), 127.6 (C), 150.6 (C). MS (*m*/*z*, (%)): 187 (10), 172 (28), 83 (24), 71 (35), 69 (44), 57 (100). Exact mass (EI): Calcd for $C_{13}H_{17}N$: 187.1361 (M^+). Found: 187.1339.

***trans*-2-Methyl-4-methyl-1,2,3,4-tetrahydro-4*H*-pyrrolo-[3,2,1-*ij*]quinoline (*trans*-3b).** ^{1}H NMR (δ, ppm): 1.11 (d, *J* 6.5 Hz, 3H), 1.15 (d, *J* 6.5 Hz, 3H), 1.76−1.89 (m, 1H), 1.96−2.08 (m, 1H), 2.54 (dd, J_1 8.5 Hz, J_2 6.5 Hz, 1H), 2.67 (t, *J* 6.5 Hz, 2H), 3.07 (dd, J_1 8.5 Hz, J_2 7.0 Hz, 1H), 3.40 (m, 1H), 3.86 (m, 1H), 6.54 (t, *J* 7.5, 1H), 6.80 (d, *J* 7.5 Hz, 1H), 6.88 (d, *J* 7.5 Hz, 1H). ^{13}C NMR (δ, ppm): 16.9 (CH_3), 17.2 (CH_3), 22.9 (CH_2), 31.0 (CH_2), 37.5 (CH_2), 46.5 (CH), 57.3 (CH), 117.5 (CH), 118.7 (C), 122.5 (CH), 126.5 (CH), 127.9 (C), 148.4 (C). MS (*m*/*z*, (%)): 187 (7), 172 (26), 125 (22), 123 (38), 119 (31), 97 (66), 83 (67), 71 (43), 69 (91), 57 (100). Exact mass (EI): Calcd for $C_{13}H_{17}N$: 187.1361 (M^+). Found: 187.1339.

Results and Discussion

To ascertain whether **1a**−**c** exhibit a photochemical behavior similar to that of the more simple 2-allyanilines, they were irradiated using 254- or 300-nm light, in acetonitrile solution, under argon atmosphere. The photoproducts were isolated by column chromatography. They were found to be the *cis*- and *trans*-lilolidines **3** (Chart 1); their stereochemical assignment was achieved by means of NOE experiments.

The photoproducts distribution after 30 min irradiation is summarized in Table 1. In the cases of **1b** and **1c**, a mixture of *cis*- and *trans*-lilolidines was obtained; the diastereomeric excesses (de) were low. Figure 1 shows the photoreaction

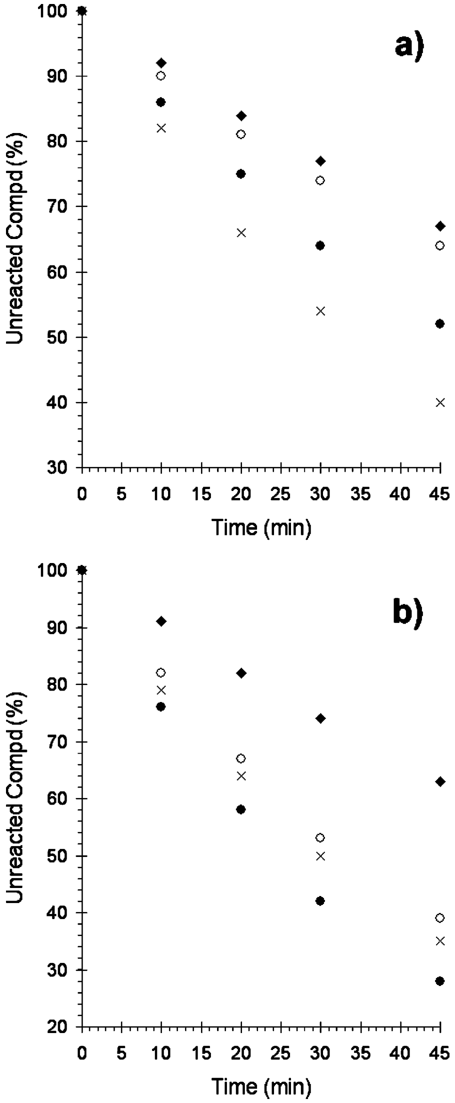


Figure 1. Photoreaction kinetics of **1a** (×), **1b** (○), **1c** (●), and 2-allylaniline (◆) using (a) 254 nm and (b) 300 nm.

TABLE 1: Photoproducts Distribution Found for the Irradiation of 1a−c

compd	λ (nm)	conv. (%)	products (%) *cis*-3	products (%) *trans*-3	de (%)
1a	254	46	100		
1b	254	26	52	48	4
1c	254	36	61	39	22
1a	300	50	100		
1b	300	47	50	50	0
1c	300	58	51	49	2

kinetics of compounds **1a**−**c**. The corresponding data for the related compound 2-allylaniline are included for comparison. In general, the photoreaction quantum yields were low (0.15 ± 0.05 at 254 and 300 nm). This was specially the case at wavelengths longer than 300 nm (ϕ < 0.05 at 335 nm).

After the realization that **1a**−**c** exhibit a 2-allylaniline-like photochemical behavior, the photophysical properties of these compounds were studied, in the search for experimental evidence in favor of an intramolecular NH/π interaction in the ground and/or the excited state.

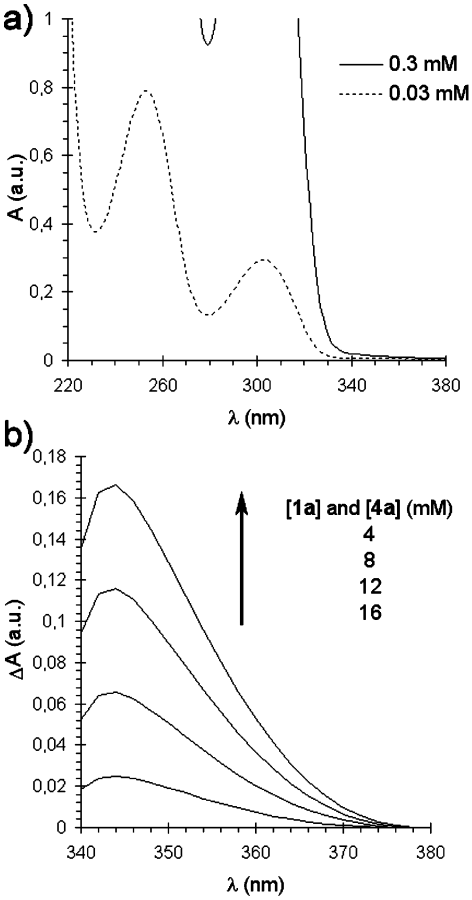
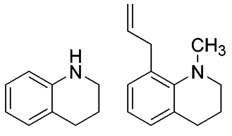


Figure 2. (a) Absorption spectra of **1a** in acetonitrile at 0.3 and 0.03 mM concentrations; (b) subtracted UV spectra (**1a**−**4a**) in the long-wavelength region.

CHART 2



4a **5a**

Figure 2a shows the ultraviolet absorption spectra of **1a** at two different concentrations (0.3 and 0.03 mM), which present two maxima at around 250 and 300 nm. Besides, a tail extending until ca. 380 nm was distinguishable in the case of the more concentrated solution. In principle, this long-wavelength absorption could be attributed to a ground-state NH/π complex. To check this hypothesis, the absorption spectra of **1a** were recorded at different concentrations and compared with those of 1,2,3,4-tetrahydroquinoline (**4a** in Chart 2), which lacks the allyl substituent, at the same concentrations. The subtracted spectra (**1a**−**4a**) are given in Figure 2b. They clearly show a well-defined emerging band with maximum at 340−350 nm.

The fluorescence spectra of **1a** were obtained both by excitation at the maximum (300 nm) and at the long-wavelength band (330 nm). Remarkably, the emission λ_{max} was strongly dependent on the excitation wavelength (Figure 3). The appearance of the 420-nm band, strongly red-shifted with respect to the usual emission of anilines (320−350 nm), could in principle be attributed to the excited complex AB*.[23]

As the emission exhibited a marked dependence on the excitation wavelength, full excitation spectra were recorded; they are shown in Figure 4. Interestingly, while the excitation maximum for the species emitting at 360 nm was essentially coincident with the main absorption maximum shown in Figure 2a, the excitation spectrum obtained for the emission at 420 nm closely matched the long-wavelength absorption observed in Figure 2b. This confirms the formation of a ground-state

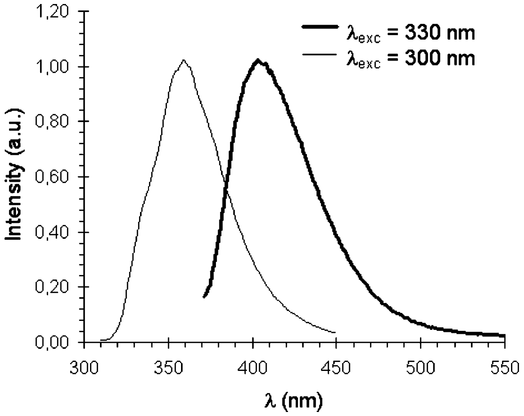


Figure 3. Normalized emission spectra of **1a** in acetonitrile, exciting at λ = 300 and 330 nm.

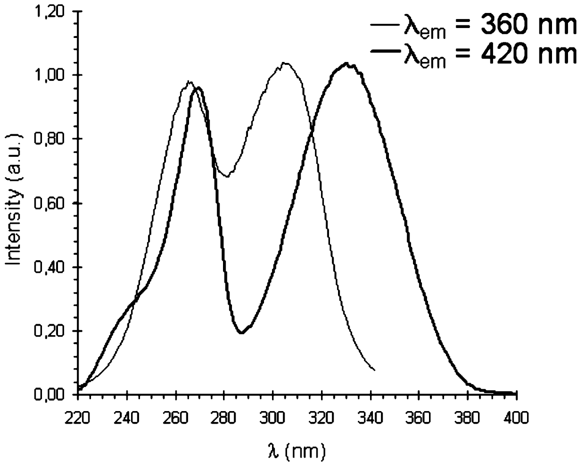


Figure 4. Normalized excitation spectra of **1a** in acetonitrile, for emissions at λ_{max} = 360 and 420 nm.

complex, present in minor amounts, that upon light absorption generates the corresponding excited species.

Analogous fluorescence studies were performed for **1b** and **1c**. Figure 5 shows the emission spectra of both compounds, using 300 and 330 nm as the excitation wavelength. Again, two distinct bands were observed. Their excitation spectra were different (Figure 6), as expected for the existence of two different species in the ground state. Thus, the behavior of **1b** and **1c** was similar to that stated above for **1a**. On the basis of the existing background, our assumption was that the intramolecular interaction in AB and AB* was of the NH/π type. To verify this assumption, parallel studies were performed on two model substrates, namely, **4a** and **5a** (Chart 2). Thus, the parent 1,2,3,4-tetrahydroquinoline (**4a**) would allow us to determine the role of the allyl group. On the other hand, 8-allyl-*N*-methyl-1,2,3,4-tetrahydroquinoline (**5a**) would be an adequate substrate to ascertain whether the free NH group is required for complex formation.

The UV spectra of **4a** and **5a** (Figure 7) were similar to that of **1a**, with maxima around 250 and 300 nm, but with a markedly lower absorption at longer wavelengths. The fluorescence spectra were meassured by exciting at 300 and 330 nm. As expected for the lack of NH/π interaction, no emission resulting from excitation of a ground-state complex was detected for these model compounds (Figure 8).

To rule out that the observed band at 340−360 nm could be the result of two overlapping emissions, excitation spectra were recorded at different λ_{em} for **4a** and **5a**. As shown in Figure 9, no evidence for a ground-state complex was obtained.

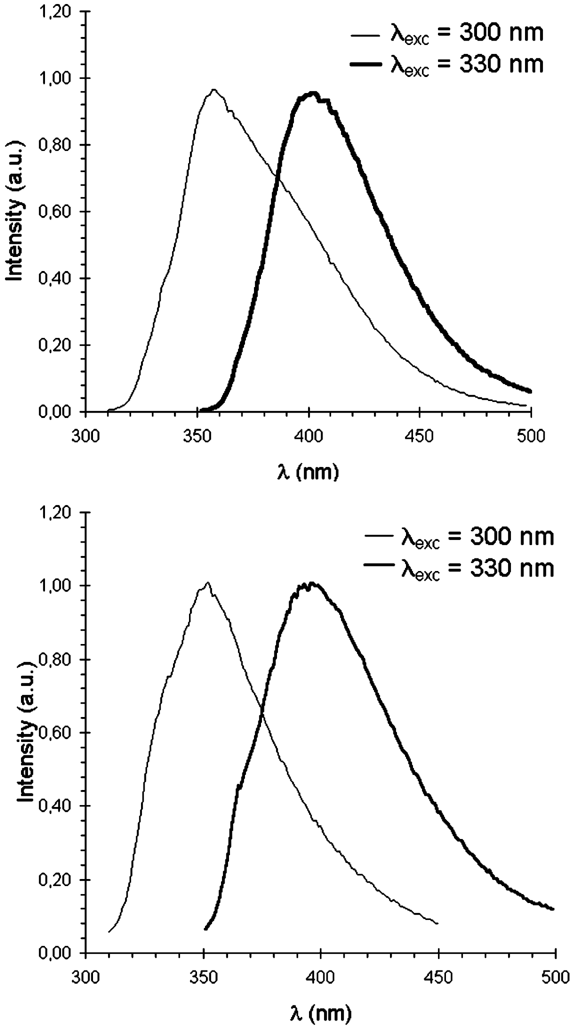


Figure 5. Normalized emission spectra of **1b** (top) and **1c** (bottom) in acetonitrile, exciting at λ = 300 and 330 nm.

These experimental results with **4a** and **5a** confirm that both the NH group and the olefin are necessary for formation of the ground-state complex observed for **1a**−**c**.

The intramolecular NH/π interaction was theoretically studied in **1a** using quantum-chemical calculations[19] at the B3LYP/6-31G** computational level.[18] Two structures (**I** and **II** in Figure 10) were optimized: in **I**, the allyl substituent displays an extended arrangement relative to the benzene ring; in **II**, the sigma bonds of the allyl substituent are twisted in order to approach the π system to the amine hydrogen atom. The calculated energies are summarized in Table 2. According to the B3LYP/6-31G** method, structure **II** is 2.3 kcal/mol more stable than **I**. To confirm the DFT result, further optimizations were performed at HF and MP2 computational levels.[19] The results were close to those obtained at the B3LYP level, with **II** between 2.0 and 2.5 kcal/mol lower in energy than **I**, in agreement with a favorable NH/π interaction (see Table 2). The same trend was observed when diffuse functions were used to optimize structures **I** and **II** at the HF/6-31+G** and B3LYP/6-31+G** levels, where the energy differences were somewhat smaller (between 1.7 and 1.9 kcal/mol), although still larger than those estimated using the semiempirical perturbed configuration interaction with localized orbitals (PCILO) model for related 2-allylanilines (between 1.0 and 1.7 kcal/ mol).[11]

A detailed analysis of the geometries of **I** and **II** was performed at the three computational levels; for each structure,

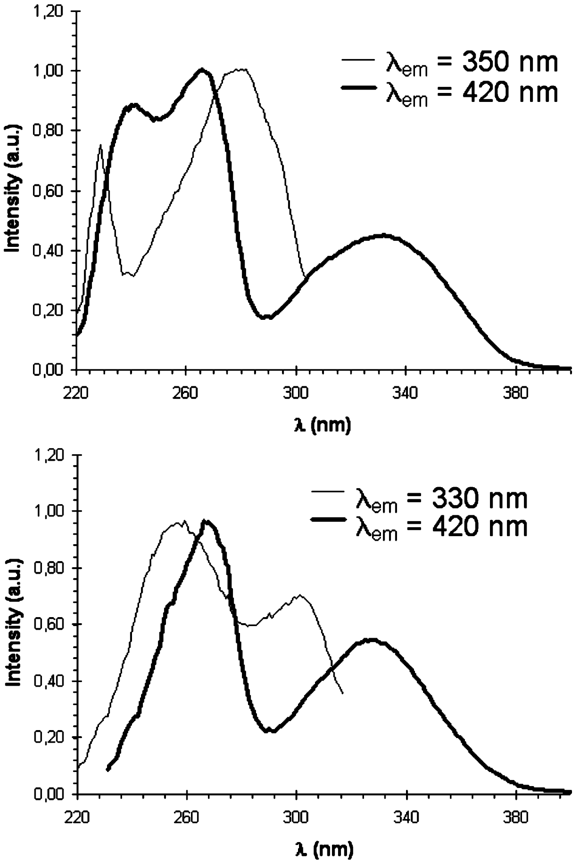


Figure 6. Normalized excitation spectra in acetonitrile of **1b** (top), for emissions at $\lambda = 350$ and 420 nm, and of **1c** (bottom), for emissions at $\lambda = 330$ and 420 nm.

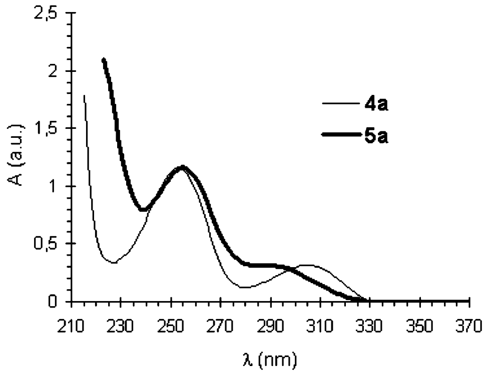


Figure 7. Absorption spectra of **4a** and **5a** in acetonitrile (0.03 mM).

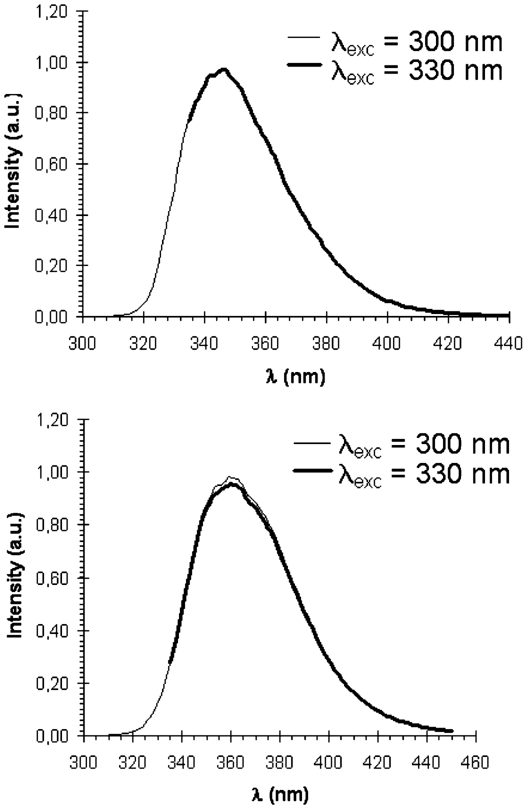


Figure 8. Emission spectra of **4a** (top) and **5a** (bottom) in acetonitrile, exciting at $\lambda = 300$ and 330 nm.

TABLE 2: Total (au) and Relative (kcal/mol, in parentheses) Energies of Structures I and II

	I	II	
HF/6-31G**	−517.610065	−517.613309	(−2.0)
HF/6-31+G**	−517.622489	−517.625136	(−1.7)
B3LYP/6-31G**	−521.068650	−521.072260	(−2.3)
B3LYP/6-31+G**	−521.086983	−521.089951	(−1.9)
MP2/6-31G**	−519.403955	−519.407946	(−2.5)

the differences associated with the employed methodology were very minor. The allyl substituent in **I** is positioned perpendicular to the aromatic plane (see Figure 10), with the C═C double bond in an eclipsed arrangement relative to the benzylic hydrogens, positioned far from the amine. In **II**, the $CH_2-CH=$ single bond is twisted ca. 120° (relative to that of **I**), and the distances between the amine hydrogen atom and the $CH_2=$ and $CH=$ carbon atoms are 2.62 and 2.47 Å, respectively. In **I**, the shortest distance between the amine hydrogen and the olefinic carbons is 2.70 Å. For the relevant dihedral angles of both structures, see Figure 10. Inclusion of diffuse functions at the B3LYP/6-31+G** level increases slightly the distances between the amine hydrogen atom and the $CH_2=$ and $CH=$ carbon atoms of **II** to 2.76 and 2.58 Å, respectively.

The spectroscopic properties of the two structures were evaluated computing the first singlet excited state, using the TD[22] approach at the B3LYP/6-31G** level. The resulting vertical excitation energies were 105.3 kcal/mol (for **I**) and 100.6 kcal/mol (for **II**). Without overemphasizing the quantitative value of these energies that do not take into account the temperature and solvent effects, nor the geometry changes in the excited state, it is interesting to note that they are in qualitative agreement with the experimental results: the NH/π interaction existing in **II** produces a decrease of the energy required for vertical excitation.

Conclusion

Photophysical studies performed on 8-allyl-1,2,3,4-tetrahydroquinolines **1a**−**c** demonstrate the formation of a NH/π intramolecular ground-state complex (AB). Excitation of this complex, which can be achieved at long wavelengths (330−340 nm), gives rise to the corresponding excited species AB*. Emission from AB* is red-shifted (420 nm) with respect to that observed when the monomer A is excited ($\lambda_{exc} = 300$ nm). This is supported by theoretical DFT studies that reinforce the conclusions drawn from previous semiempirical PCILO calculations and provide estimation on the vertical singlet−singlet excitation that are in reasonable agreement with the experimental data.

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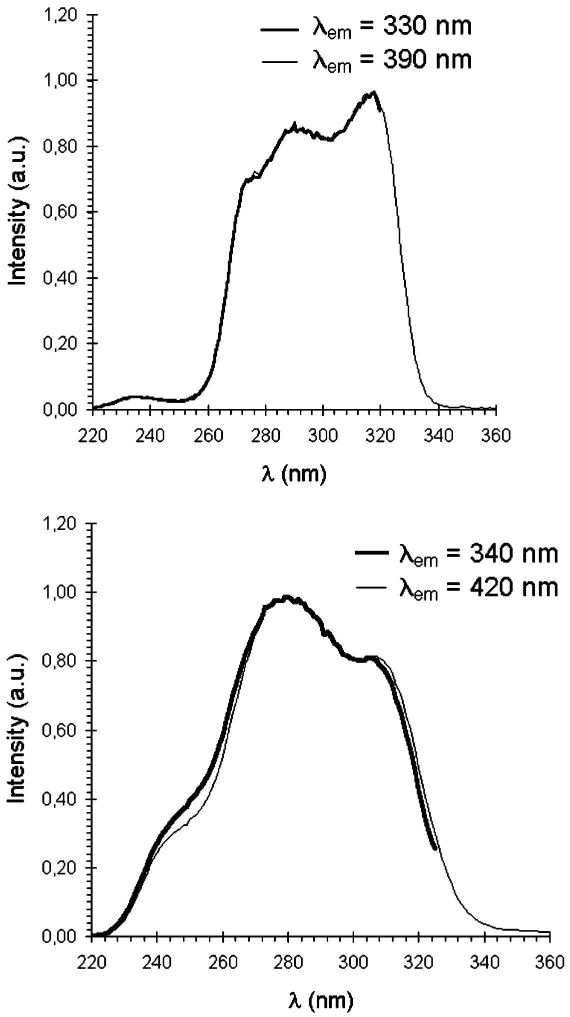
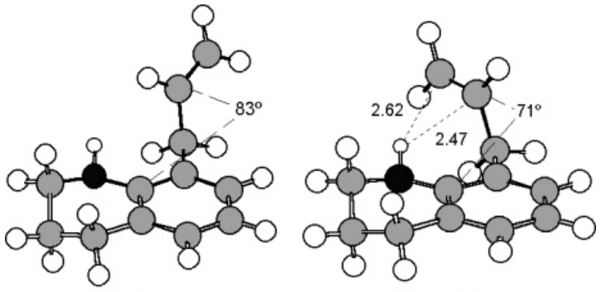


Figure 9. Excitation spectra in acetonitrile of **4a**, for emissions at $\lambda = 330$ and 390 nm (top), and of **5a**, for emissions at $\lambda = 340$ and 420 nm (bottom).



I **II**

Figure 10. B3LYP/6-31G**-optimized geometries for the structures **I** and **II** of **1a**.

(Grupos 03/82), and the Universidad Politécnica de Valencia (fellowship to E.A.L.) is gratefully acknowledged.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **1b**, **2b**, ***cis*-3b**, and ***trans*-3b**; relevant NOE interactions for assignment of ***cis*-3b** and ***trans*-3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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